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AN AB INITIO STUDY OF THE CRYSTALLINE
STRUCTURE OF SULFURIC ACID (H_2SO_4)-
THE POINT CHARGE MODEL

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To my wife Laura and our first child

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STRUCTURE OF SULFURIC ACID (H_2SO_4)-
THE POINT CHARGE MODEL

by

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ABSTRACT

The point charge model is used to calculate the crystal structure of sulfuric acid (H_2SO_4) with the 6-31G** basis set. The point charge model accurately reproduces the structural trends which occur in transforming from the gas to the solid phase. The calculated crystal structure of sulfuric acid is in reasonably good agreement with both the X-ray and neutron-diffraction structures.

The point charge model is shown to precisely simulate the deformation forces which are present in the solid upon crystallization. The point charge model exhibits a definite shift of electron density from the bridging hydrogens to the acceptor atoms, identical to those found in other ab initio studies. The calculated crystal structures are insensitive to the magnitude of the point charges.

Two new iterative techniques, using the point charge model, are introduced which give superior results to any of the single optimization cycle methods. These iterative techniques account for any forces which are not electrostatic by nature.

The gas phase structure of H_2SO_4 is optimized using the STO-3G*, 4-31G**, and 6-31G** basis sets. Comparisons are made between the programs TEXAS, TEXAS(D), and Gaussian-82.

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CHAPTER ONE

INTRODUCTION

Over the years, many researchers have shown the ability to apply quantum theory to chemistry in order to supplement experimental results. However, it has only been in the past decade with the great advances in computers coupled with the development of efficient algorithms that ab initio calculations have become practical on molecules of more than a few atoms.

The term "ab initio" is frequently cited in the literature but rarely defined. Ab initio calculations can basically be thought of as those which treat all the electrons and do not utilize parameters which are fit to experimental data as compared to semi-empirical calculations. For example, a Hartree-Fock calculation of a restricted closed-shell single determinant wave function is one in which no approximation is made to the integrals or the electronic Hamiltonian. However, it is completely specified by the choice of a basis set and the coordinates of the nuclei.[1]

One area in which ab initio calculations have been particularly successful is in evaluation of molecular structure. The theoretical determination of a molecular structure involves minimizing the total energy of the molecule with respect to simultaneous variation of the internal coordinates.[2] The application of this procedure to complex molecules became practical only after the introduction of the gradient method by Pulay. This method greatly reduced the time to calculate an optimum geometry especially for large molecules.[3] The resulting optimized structure has a known basis set dependance which results in a constant error for a

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given parameter called the offset value. This offset value is reasonably constant over a wide range of molecules.[4] Boggs and coworkers have reported extremely accurate structures by combining experimental and theoretical data. The structures presented in their study are more accurate than either theoretical or experimental techniques could produce alone.[5] Not only have ab initio calculations been able to accurately reproduce experimental bond lengths, bond angles, and conformations but in some cases ab initio calculations have actually shown where experiments have determined incorrect structural parameters. Although the latter is the exception, it shows both the value and validity of ab initio calculations as a supplement to experimental data.

The ability to determine accurate molecular structures is the key to many areas of chemistry. The structure of a molecule not only defines its physical properties but also influences how it reacts with other molecules. This information is vital to such diverse areas as the development of "stable", powerful explosives and propellants, the synthesis of effective catalysts, the understanding of how enzymes with only specific structures can fit into certain substrates, the determination of complex reaction mechanisms, and the production of superconductors. However, to a chemist, the most fundamental concern which structural information can shed light on is chemical bonding.[6] The understanding of chemical bonding is fundamental to all areas of science.

One area in which there is a great deal of interest is the structural differences which occur in some molecules. These differences can be between the same type of bond (eg, C-H) or functional group (eg, CH_3) over a variety of similar compounds with different substituents. These changes can also occur within the

same molecule when it is in a different phase or chemical environment (eg, in solution). These structural differences need not be large to be important. In fact, they can be very small. Differences on the order of 0.01 Å in a bond length or a couple of degrees in a bond angle may reveal extremely valuable structural information if they are reliably determined. However, only real structural differences should be considered and any apparent differences which are detected must be eliminated if meaningful comparisons are to be made.[7] Apparent differences can arise from either the particular interaction of radiation with matter or because of the vibrational averaging which occurs in a particular experiment. It is important to note that all experimental techniques produce geometrical parameters which are based on averaging of the molecular vibrations. However, at least theoretically, ab initio calculations give equilibrium intermolecular distances which correspond to the minimum of the potential energy surface and are not subject to molecular vibrations.

The vast majority of all ab initio calculations are performed on isolated "gas" phase molecules. The reason for this is quite simple - computer capacity. The most accurate results come from ab initio calculations performed with large basis sets. However, current computer capacity limits large basis set calculations to no more than about two dozen atoms. This limit of two dozen atoms with a fairly large basis set is pushing the capacity of even the Cray supercomputer. Thus, in order to conduct conventional ab initio calculations on solids, the size of the basis set would have to be greatly reduced, a lower level of theory must be used, or assumptions must be made about the symmetry of the molecule. These restrictions almost always result in less accurate molecular parameters.

The intent of my work was to study the structural changes which occur in a molecule between the gas and solid phase through the use of ab initio calculations. In selecting a particular molecule to study, I established several criteria. First, the number of atoms in the molecule must be small enough that a large basis set could be used to give accurate results but be within the capacity of the Cray supercomputer. All of the calculations in this study were performed on the Cray X-MP/24 at the University of Texas Center for High Performance Computing (UTCHPC). Second, there must be an accurate experimental determination of the gas and solid phase structure so that comparisons could be made with the calculations. Finally, if possible the molecule should be one which is of general interest. After careful consideration, sulfuric acid (H_2SO_4) was selected as the molecule to study which met all of the above criteria.

In order to reduce the calculation of solids to one that can be handled by present computers, a simpler method must be used in order to simulate the effects of the crystal lattice. The problem is basically how to accurately represent the molecular-charge distribution of the surrounding molecules in the solid. The simplest is to use the Mulliken population analysis.[8] The Mulliken population analysis comes from parameters that are already calculated in quantum mechanical calculations. The major problem with this method is that the assignment of charges to the atoms is rather arbitrary and is often very basis set dependent.[8] However, a previous study done using the Mulliken population analysis and point charges was able to accurately reproduce the crystal structure of cyanoformamide ($NCCONH_2$).[9] The purpose of my study was to apply the point charge method to a different type of molecule and to develop some new techniques in order to see

their effect. The theoretical methods used in this study are presented in Chapter 2. Chapter 2 includes not only the basis set and level of theory considerations but also a review of the various methods which have been used to simulate crystal field effects. Chapter 3 contains the sulfuric acid results including the optimized gas phase geometry and the various techniques used to calculate the solid geometry. Chapter 4 presents my conclusions and suggestions for future studies.

CHAPTER TWO

METHODS

In any ab initio calculation, the selection of the basis set and the level of theory are crucial. A decision must be made between the computational cost and the desired accuracy. Obviously, the most accurate results are desired from any calculation. However, a structure accurate to 0.01 Å at one-hundredth the cost of one which is accurate to 0.001 Å maybe preferred if the first structure demonstrates the effects which are being studied. Although, this is a hypothetical example, it points out the importance of extremely careful selection of the basis set and level of theory. In my particular study, the selection of a method to simulate the crystal-field effects is also a major factor. Again, selection involves a compromise. In this case, a compromise must be made between computational cost, accuracy, and ease of implementation. In this chapter, I will discuss the various methods used in this study. The level of theory and basis set are discussed first, followed by the crystal-field simulation method. Finally, I will discuss the convergence criteria used in this study.

LEVEL OF THEORY AND BASIS SET SELECTION

The ultimate goal of quantum chemistry is the calculation of the solution to the Schrödinger equation resulting in an exact molecular wave function. However, that requires an infinitely large basis set expansion of the wave function along with the implementation of full configuration interaction. This is clearly an unattainable goal. In actuality, the basis set is truncated to a finite size and the electron correlation, if treated at all, is limited to a few configurations. These specifications

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define a theoretical model within which all structures, energies, and other physical properties can be studied.[10] While proper selection of the model is important, recognizing and understanding the limitations of the given model on the results is imperative.

The main sources of error in any geometry optimization using the gradient method are neglect of electron correlation (where it is either ignored or incompletely treated) and the use of a finite basis set. The combined effect of these errors on the results obtained from a computed molecular structure are shown in Figure 2-1. The figure depicts the error in some arbitrary structural parameter (such as a C-H bond) in a variety of molecular environments plotted against increasing basis set size. When an infinite basis set is used (the Hartree-Fock limit), the error due to the neglect of electron correlation is found to be remarkably constant for the given parameter over a wide range of molecules. For much smaller basis sets, the error is expected to fall within the shaded area. However, at some point (X), the basis set is sufficiently large that the scatter in the calculated parameter is extremely small. This results in a constant known error for the given parameter called the offset value. The remaining absolute error is due to the truncation of the basis set and the neglect of electron correlation. Thus, the major flaw with small basis sets is the inconsistency of the error.[4]

In order to keep the computational costs low for large molecules, the calculation should be performed as close as possible to the point X. Any increase in the basis set results in an increase in computation time and disk storage space proportional to the fourth power of the number of basis functions (N^4). Beyond point X, the wave function approaches the Hartree-Fock limit where only electron

Figure 2-1[4]
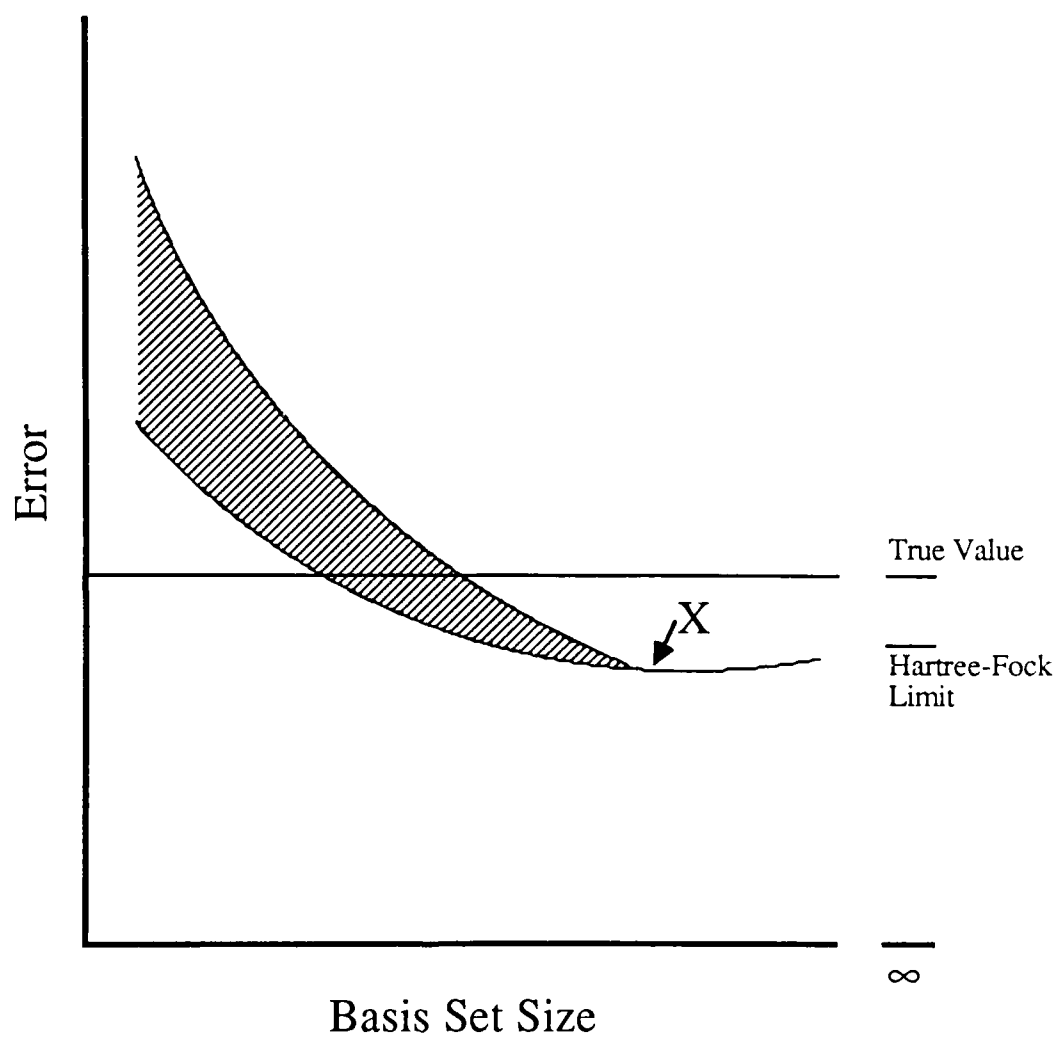
correlation error remains. The incorporation of any high-level electron correlation treatments results in a large increase in computation time and disk storage roughly proportional to n^6 where n is the number of electrons in the molecule.[11] Even the most efficient correlation methods, such as the local correlation method[12], are two to three times more expensive than a single determinant calculation. Therefore, depending upon the size of the molecule and the number of basis functions, the treatment of electron correlation may be prohibitively expensive for a given molecule.

Based on the above observation, calculations can be done efficiently at point X. For many structural parameters, point X corresponds to approximately double zeta basis sets. However, for some parameters such as torsional angles around nitrogen or oxygen, it is essential to add at least one set of polarization functions to the basis to reach that point. The offset value for most bond angles is zero using this basis set. However, bond distances have non-zero offset values at this level and for some types of bonds the basis set must go beyond double zeta.[13] A common misconception is that the addition of d orbitals (polarization functions) to first and second row elements is incorrect since d orbitals in these elements are not actually occupied. The addition of polarization functions is only done to allow greater flexibility in the description of the bonds. Their addition does not imply that d orbitals are actually involved in the formation of these bonds.

Because of the size of the H_2SO_4 molecule, the treatment of electron correlation is prohibitively expensive. Unless stated otherwise, the calculations in my study were completed at the single determinant level using the gradient program TEXAS[14] with no symmetry restrictions. During the course of my study, Pulay's

group completed a new version of TEXAS which was used for a few additional calculations. The major improvements are increased speed and the ability to use true Gaussian d functions. After some optimization of the program by Cordell for the Cray, I have seen up to a 30% increase in speed over the old version of TEXAS. The inclusion of true d functions has replaced the use of displaced p functions which were used to construct d functions in the previous version of TEXAS. Throughout this paper, the new version of TEXAS will be referred to as TEXAS(D).

As stated earlier, one of the most important parts of any ab initio calculation is the selection of a basis set. The literature is inundated with almost 100 basis sets[15] which range from the minimal STO-3G basis set to very extensive triple zeta plus multiple polarization function basis sets. Thus, the selection of a basis set for a particular problem must be made based on the ab initio program used, the accuracy required, and how much computation time is available. The TEXAS program efficiently uses split valence shell basis sets where the s and p Gaussian exponents are equal. Pople's 6-31G** basis sets are used almost exclusively throughout this study.[16,17,18,19,20] Some calculations, which will be specifically mentioned, were completed using a 4-31G** basis set on sulfur[21] with a 6-31G** basis set on oxygen and hydrogen (referred to throughout the remainder of this paper as 4-31G**). The asterisks in the notation for the basis sets refer to the inclusion of polarization functions. The first asterisk refers to the addition of d functions to the heavy atoms sulfur (exponent=0.65)[17] and oxygen (exponent=0.8)[22]. The second asterisk refers to the addition of p functions to hydrogen (exponent=1.1)[22]. As discussed earlier, the inclusion of polarization

functions is essential to accurately obtain torsional angles around oxygen. Another basis set which was used to study the sulfuric acid dimer was Pople's STO-3G*.[23] That basis set consists of the minimal STO-3G basis with the addition of five d functions only to second row atoms.

METHOD TO SIMULATE CRYSTAL-FIELD

Numerous studies have been made in order to apply ab initio calculations to solids. One reason is the advantages which ab initio calculations offer over some experimental methods. While X-ray and neutron diffraction provide valuable information about the spatial arrangement of the atoms in molecules and the packing of the molecules in lattices, they tell us nothing of the forces which determine the crystal structure. In addition, they give no information on why the molecules pack in the observed space group or the influence of crystal forces on the conformation of flexible molecules.[24] In some cases the experimental methods cannot "locate" particular parts of a molecule, especially hydrogens. In the case of sulfuric acid, three X-ray diffraction studies, with the latest being done in 1978, could not "locate" the hydrogens. It was not until a neutron diffraction study was done in 1983 that the hydrogens were located. Another problem with the experimental data is the vibrational averaging which is inherent to all experimental methods. It is these questions and others to which ab initio calculations can be directly applied.

One area in which theoretical methods have been frequently applied is the study of hydrogen-bonding. The ab initio methods which have been used range from the complex use of an atom-centered multipole expansion[25] to the simple point charge model.[9] It was not until the study by Saebø, et al. that the influence of crystal forces on the intramolecular geometry was studied in detail. Saebø reported

impressive agreement between X-ray diffraction and calculated structural parameters by using point charges based on a Mulliken population analysis. Regardless of the methods which have been used, the importance of the electrostatic interaction energy in determining the energetically most favorable geometry is well established.[8,9,24,26,27] In fact, it led Bonaccorsi, et al.[28] to the "electrostatic assumption". Bonaccorsi and coworkers postulated that the minima in the total interaction energy coincide with those in the electrostatic energy for rotational degrees of freedom.[28] Thus, it is clear that approximating the electrostatic energy via a model can reveal valuable molecular structure information if the model is sufficiently detailed.

One study which specifically considered crystal-field effects was the calculation of the rotational conformation of acetamide.[29] In that case, the crystal structure had shown that the torsion angle was between 0° and 30°. However, several attempts by other authors to compute the lattice energies and total crystallographic conformational energies (lattice+torsional) could not account for that torsional angle. A procedure was developed to compute the lattice energy as the sum of three long-range contributions (electrostatic, polarization, and dispersion) and a short-range repulsive contribution. That procedure yielded a minimum lattice energy with a torsional angle between 0° and 30° as observed in the crystal structure.[29] Similarly, through the use of calculated electrostatic molecular potentials, researchers were able to compute the preferred arrangement of linear chains of formamide molecules as observed in the crystal.[30]

The combination of experimental and theoretical methods has been used in several studies. One study of hydrogen bonding, crystal packing, and the effect of

crystal forces on the molecular conformation of amides and carboxylic acids expounded upon the "marriage" of X-ray diffraction and ab initio calculations.[24] The goal of that study was to obtain a general force field for organic and biological molecules. In that study, the lattice energy was calculated as a sum of the Lennard-Jones potential and the Coulombic interaction. The researchers were able to use their procedure to explain the crystal-packing mode of formic and acetic acid. Their study clearly showed that the electrostatic interactions were the overriding factor in determining the particular packing occurring.[24] In another "marriage", experimental electron densities were combined with calculations in order to study the role of Coulomb forces in the crystal packing of amides. In this case, the researchers were able to use the Coulomb interaction energies in order to determine the possible and preferred molecular packing modes. In addition, they were able to obtain reliable estimates of the van der Waals atom-atom potential parameters using the calculated Coulomb energies.[27]

In one investigation, the electrostatic energy in the formic acid crystal was studied.[26] The geometry of formic acid was not optimized; instead the researchers used the experimental gas and crystal geometries to conduct their study. In their study, two approaches were pursued - multipole and point charge lattice sums. In the multipole method, the electrostatic energy is expanded in a series to yield the various multipole moments. That particular study used multipole moments up to the sixth moment. The electrostatic energy then becomes a sum of the interaction energy between the polar multipole moments. In the point charge method, the charge distribution is represented by a set of point charges which were obtained from a Mulliken population analysis. The electrostatic energy simply reduces to the

sum of the interaction energy between the point charges. Several important conclusions were made from the results. First, the electrostatic portion of the lattice energy of formic acid was both large in magnitude and varied strongly with the orientation of the molecule. Several orientations, including the one observed experimentally, were found to minimize the electrostatic energy. The location of these minima were dictated by interactions with nearest-neighbor molecules. Second, the point charge method agreed qualitatively with the multipole series for the dependence of the electrostatic energy on the molecular orientation. Finally and most importantly, the electrostatic component of the lattice energy was found to act as the driving force for molecular distortion upon crystallization.[26]

The conclusion which can be drawn from all of the above studies is that theoretical calculations can give extremely valuable information about a wide variety of crystal parameters. However, it is now time to specifically address the crystal parameter which is of interest in my study - molecular structure. A straightforward approach which has been applied to the calculation of molecular structure is to compute it directly in the solid. This involves selecting a model of an extended "supermolecule" that is sufficiently large to represent the condition existing inside the crystal. That same method has been previously used to study such phenomena as the adsorption of a gas on a surface, where the solid is represented by a small number of atoms. One way of implementing this method is to consider all the molecules within a unit cell as the "supermolecule" and then impose boundary conditions to correct for effects at the cell edge. However, as the size of the molecular system increases, the accuracy of the computed results suffers. As a result, the "supermolecule" method has not been conducive to highly accurate

results for molecules of appreciable size.[4] A recent study using that method has been completed by Cordell and Boggs on furan molecules.[31] The calculations were done on furan dimers and trimers located in the spatial orientation found in the crystal. Their study was able to show which neighbor molecules stabilized the crystal structure and to what extent. The interaction energies of the various subsets of the unit cell were shown to be essentially additive, with the packing forces expected to decrease the calculated crystal stabilization by 5 to 10%. In addition, they concluded that the short C=C bond length reported for the crystal was an artifact of the X-ray diffraction experiment.[31] However, as stated earlier, the "supermolecule" technique is only useful for relatively small molecules. There is also an appreciable cost associated with it which increases as N^4. Thus, large basis set and/or large molecule calculations using the "supermolecule" concept are very expensive.

Based on the previous discussion, there are major problems which afflict many of the methods which have been used to simulate crystal-field effects. All of the above methods suffer from one or more of the following problems: high computational cost, low accuracy, or difficulty in implementation. Recently, a method has been proposed by Saebo, et al. to calculate crystal structures which seems to overcome these problems. Their study consisted of investigating the geometry changes which occur in cyanoformamide in going from the gaseous to the solid states, with emphasis on the effect of the crystal forces on the intramolecular geometry. Their approach consisted of using a simple point charge model to simulate the crystal-field effects. First, the geometry of the free molecule was optimized and a wave function obtained. Next, a Mulliken population analysis was

run to generate the magnitude of the point charges. The point charges were then placed around the free molecule in the spatial arrangement which corresponded to the previously determined X-ray diffraction structure. Since the hydrogens were not located in the X-ray diffraction experiment, the N-H bond distances were set to 1.0 Å. Finally, the geometry of the free molecule was optimized inside of the point charges. The resulting optimized structure yielded bond lengths and bond angles with a maximum deviation of 0.011 Å and 0.4°, respectively, compared to the X-ray diffraction structure. The major advantages of their method were not only the accurate results and the ease of implementation but also the very slight increase in computation time compared to the free molecule. The small increase in computation time was only due to the increase in the number of one-electron integrals and nuclear repulsion terms.[9] Thus, their method appears to possess all the advantages of the previously discussed methods with none of the disadvantages.

There are a few problems with the point charge model which need to be considered. The model assumes that the crystal-field effects can be simulated through purely electrostatic interactions. However, these are not the only forces which bind molecules together in solids. In order to fully understand the types of forces which bind crystals together, the various crystals which exist must be reviewed. There are basically four types of crystals - ionic, covalent, metallic, and molecular. Metals represent a special class of solids and will not be discussed further. In ionic crystals, the atoms are bound together by largely electrostatic forces and there is no such thing as an individual molecule. Covalent solids are actually one huge molecule which is composed of covalently bonded atoms. The atoms are held together by sharing electrons with their neighbors. On the other

hand, molecular crystals actually contain a collection of distinguishable molecules which are bound together. The molecules are held together mostly by dipole interactions, van der Waals' forces and hydrogen bonds. In reality, very few crystals fall strictly into one of these categories. Instead, many crystals are held together by more than one of these forces. Not only are there numerous examples of crystals composed of both ionic and covalent bonds but even molecular crystals may contain a small amount of ionic or covalent bonding.[32] But, all of these forces share a common denominator - they all depend upon charged particle interactions. In summary, the forces which bind crystals together are very complex and in certain cases may not be fully described by only electrostatic interactions.

The foremost problem with the point charge model used by Saebø and coworkers is that it does not specifically allow for intermolecular electron transfer. The neglect of electron transfer in their method could certainly degrade the accuracy of calculated crystal structures in which covalent bonding is a major force. However, since few covalent crystals exist, their method should give satisfactory results for a wide variety of other crystals. In fact, the study by Saebø indicated that hydrogen bonding was dominated by electrostatic effects. While the neglect of electron transfer must not be forgotten when interpreting results using this method, the point charge method should produce reasonable results when applied to a large variety of crystals, especially molecular crystals involving hydrogen bonding.

There still remain a couple of problems with the Mulliken population analysis which need to be considered. First, it tends to produce charges which are rather arbitrary and basis set dependent. Any defects in the point charge model are dominated by possible errors in the magnitude of the point charges.[9] Second, since

it is based on a simplified model of describing the electron distribution, the Mulliken population analysis often yields multipole moments which are quite different than those calculated from the actual wave function.[8] Although, there are other standard population analysis methods such as that of Löwdin, they suffer from the same disadvantages.[1]

In order to obtain more accurate charges, a different method has been recently proposed.[8] In that method, the molecular electrostatic potential evaluated at points in space around the molecule is used as a guide and is then fit to the point charge models. The procedure provides for selected restraints on the calculated dipole or quadrupole moments, and for the use of additional point charges to represent lone pairs in the molecule. That study found very good agreement with experimental enthalpies of formation for hydrogen bonding on nucleic acid pairs. Based on the above results, the researchers found their method superior to the Mulliken population analysis. Even given a set of point charges which accurately reproduce the molecular electrostatic potentials, it is not a trivial task to determine a set of nonbonded parameters that can be used with the charges to give good geometries.[8] This method also tends to assign larger absolute values of charge to the atoms compared to the Mulliken population analysis. However, ease of implementation was the overriding factor in choosing between these two methods. While their method may produce a more accurate point charge model than the Mulliken method, it is by no means a trivial task to implement their method. The method which provides the best compromise based on the selection criteria is the point charge model using the Mulliken population analysis.

Both versions of TEXAS have been modified to accommodate the point

charge model. The programs require that the point charges be input in Cartesian coordinates with their associated net charge. The energy which is calculated excludes the point charge-point charge interactions but includes the point charge-molecule interactions. Therefore, the calculated energy accurately shows the stabilization of the crystal when compared to the free molecule energy.

The major reason that the Mulliken population analysis is easy to implement is because the required parameters are already calculated in any standard SCF program. The only required parameters are the atomic number, the density matrix (P), and the overlap matrix (S). The number of electrons that are associated with any basis function is simply the diagonal element of the product of the density and overlap matrices which corresponds to that basis function. The corresponding number of electrons that are associated with a given atom in a molecule is obtained by summing over all basis functions on that atom. This assumes that all the basis functions are centered on atomic nuclei. The net charge of any atom (point charge magnitude) is simply the difference between the charge of the atomic nucleus and the number of electrons associated with that atom. The net charge is positive if the number of electrons associated with the atom is less than the nuclear charge and negative otherwise. Although this method is simple, it must be remembered that there is no unique definition of the number of electrons that are associated with a given atom or nucleus in a molecule. In the case of CH_4, the Mulliken population analysis results in a net charge on hydrogen which is double that given by the Löwdin method at the STO-3G level (0.06 and 0.03, respectively). The basis set used also has a profound effect on the net charge which results. A Mulliken population analysis on CH_4 gives hydrogen a net charge of 0.06 at the STO-3G

level but 0.12 at the 6-31G** level.[1] Despite its drawbacks, the Mulliken population analysis is readily obtained and has been shown to give exceptional results.

As discussed previously, the method employed by Saebø, et al. was simply to optimize the free molecule surrounded by the point charges. They chose to place the point charges in positions as determined by X-ray diffraction and to assign them net charges based on a Mulliken population analysis of the optimized free molecule. Despite their convincing results, they suggested two improvements within the frame of their model. The first was to introduce the new net charges calculated for the free molecule in the surrounding point charges. Secondly, they recommended increasing the size of the basis set.[9] These questions and several others are the focus of my study.

Based upon the suggestions of Saebø and coworkers, the expansion of the basis set by inclusion of polarization functions is a logical extension of their work. The increased flexibility offered by the polarization functions is an improvement in the basis set over that used in their study. Also, the idea of introducing the new point charge values calculated from the free molecule suggests an iterative approach to me. Although Saebø and coworkers envisioned only one additional optimization cycle, I felt that multiple optimization cycles would allow more flexibility in the model by allowing it to dynamically change. The iterative technique was applied in my study by optimizing the free molecule inside the point charges based on both X-ray and neutron diffraction structures. Then the net charges were recalculated by running a Mulliken population analysis on the new "free" molecule geometry. The new net charges were assigned to the experimental point charge locations and the

cycle was repeated until the free molecule converged in both structure and energy. This should eliminate some of the error associated with the Mulliken population analysis.

One problem with the Saebø method is that it requires a detailed experimental structure of the solid. While X-ray diffraction structures are available for a wide range of compounds, they quite often are unable to locate the hydrogens which was the case for both cyanoformamide and sulfuric acid. Then, in order to implement their method, the positions of the hydrogens must be assumed which certainly could have profound effects on the results. In addition, experimental results are prone to mistakes just like any other method. For sulfuric acid, the early X-ray diffraction results determined the symmetry to be C_{2v} instead of the actual C_2. Therefore, it would be helpful to have a method which was not quite so dependent on the experimental results.

One solution is to position the point charges based upon the free molecule instead of the experimental structures. The coordinates of the free molecule can easily be converted from Cartesian to fractional coordinates and then used to generate the point charges. That requires only the cell dimensions and the space group of the crystal and it preserves the internal geometry of the free molecule. These parameters can be determined from experiment, assumed from similar crystals, or simply guessed. This would permit calculations on molecules for which there are no experimental results or for which incomplete crystal structures exist. However, the major advantage of my method would be for calculations on molecules where the electron density is shifted away from the nuclear center and for which only X-ray diffraction crystal structures exist. One of the disadvantages of

X-ray crystallography is the fact that it gives bond lengths which are not very accurate. That is due to the manner in which X-rays interact with matter. The interatomic distances determined by X-ray diffraction represent the distance between centers of electron density and not nuclei. In molecules of this type, X-ray diffraction can give results for bond lengths which greatly differ from the true bond lengths.[7] The error in bond length could cause profound effects on the structure calculated in the point charge model. The technique of basing the point charges on the free molecule has been applied in my study using both the X-ray and neutron diffraction data. In these calculations, the only experimental information that was used were the cell dimensions and the space group. The calculations were repeated in an iterative manner until the "free" molecule converged in both structure and energy. By basing the point charges on the "free" molecules, any errors caused by inaccurate X-ray bond lengths should be eliminated.

Since the value of net charge determined by the Mulliken population analysis seems to be somewhat arbitrary, the structural results should have a dependence on the charges that are generated. However, it is not known whether this is a significant factor affecting the calculated structure. The dependence on the magnitude of the charges was approached in two manners. First, a Mulliken population analysis was run on both the experimental X-ray and neutron diffraction structures. That required a single point SCF calculation be done at the experimental geometry in order to generate a wave function. The resulting point charges varied by as much as 15% from those calculated for the optimized free molecule. Second, the value of the point charges was normalized to one of the previously calculated charges. This preserved the neutrality of the molecule and resulted in charges for

the atoms about double those for the free molecule. The new charges were than used to compute geometries which were compared to those calculated using the charges based on the free molecule.

Although the increased computation time required by the addition of point charges is small, on the order of 500-700 seconds per run, it would still be beneficial to limit the point charges to as few as possible. The increased computation time becomes a significant factor for the iterative methods which require up to 30 runs. In the Saebø study, the closest neighbor molecules were included. But there are obviously pieces of these molecules which are far enough away from the free molecule such that their electrostatic interaction is essentially zero. Hence, if they were not included, the computation time could be further reduced. In order to investigate the effect on the computed structure, calculations were made where only atoms within a given sphere from the center were included. Because of the requirement to maintain a neutral charge, a dummy charge was generated to make the sum of the point charges zero and it was placed in excess of 150 Å from the free molecule.

CONVERGENCE CRITERIA

The point charge calculations require a different type of convergence criteria than normal calculations on isolated molecules. This is due to the residual Cartesian forces which result from the presence of the point charges. In the point charge calculations, the optimized geometry occurs when the internal forces are small but the Cartesian forces may still be quite large.

An isolated molecule geometry is considered optimized when the following conditions are met:[33]

1. All Cartesian forces are less than 0.005 mdyne/angstrom.

2. Stretching and bending internal coordinate forces are less than 0.005 mdyne/angstrom or /radian.

3. Torsional internal coordinate forces are less than 0.001 mdyne/radian.

4. The internal force on torsional coordinates has changed sign.

Conditions 1 through 3 are the normal conditions used to determine geometry convergence. Condition 4 is absolutely essential to ensure convergence of low energy torsional and out-of-plane motions.[34] The above conditions should give convergence of calculated bond lengths to ± 0.002 Å, bond angles to $\pm 0.2°$, and torsional angles to $\pm 2.0°$.

As discussed earlier, the convergence criteria for the point charge calculations must be slightly different. For these calculations, conditions 2 through 4 above must be met with the additional requirement for all Cartesian coordinate displacements to be less than 0.0005 Å. The restriction on the change in Cartesian coordinates is based upon the work by Saebø and my review of other isolated molecule optimizations when conditions 1 through 4 were met.

CHAPTER THREE

SULFURIC ACID

One reason for the great interest in sulfuric acid is because of its presence in "acid" rain. The harmful effects of "acid" rain have been widely reported over the last decade. These detrimental effects include large fish kills, contamination of water supplies, and damage to automobile finishes. The Northeastern portion of the United States has been hit especially hard. Research has found this to be predominantly due to the increased burning of high sulfur coal in the Midwest. More recently, the effects of "acid" rain have been reported worldwide. Many old churches and monuments in Europe are rapidly being destroyed by "acid" rain. For these reasons and several others, such as the detection of sulfuric acid in the Venusian atmosphere, many studies have been done on sulfuric acid. These studies have centered on the formation and structure of sulfuric acid, especially the intermediates that are involved. Results from some of these studies have lead to an understanding of the formation of sulfuric acid and its detection in the vapor phase.

As discussed in Chapter One, sulfuric acid undergoes significant structural changes transforming from a gas to a solid. Regardless of the phase, the symmetry remains C_2. The H_2SO_4 molecule with C_2 symmetry is shown in Figure 3-1 along with the atom designations that will be used throughout the paper. These structural alterations can easily be seen in a comparison of the gas and solid structures as shown in Table 3-1. The most dramatic change is the shortening of the S-O single bond on the order of 0.05 Å. In addition, there is a noticeable decrease in the O=S=O bond angle coupled with an increase in the O-S-O bond angle. These

25

Figure 3-1

Atom Numbering Scheme for Sulfuric Acid (H_2SO_4)
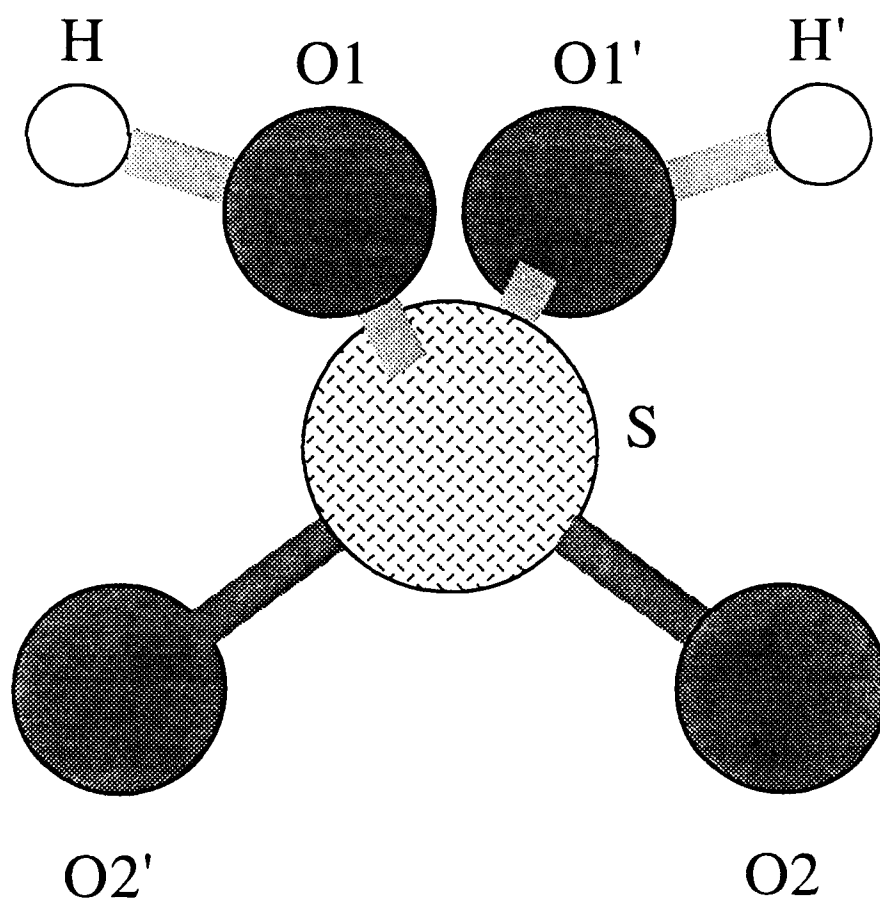
Table 3-1[a]

Sulfuric Acid (H$_2$SO$_4$) Gas and Crystal Geometries

Phase	MW[b] gas	X-RAY(1978)[c] solid	ND[d] solid	X-RAY(1965)[e] solid
S-O1	1.574±0.01	1.528(5)	1.48	1.535(15)
S=O2	1.422±0.01	1.419(5)	1.49	1.426(15)
O1-H	0.97±0.01	f	0.91	f
∠H-O1-S	108.5±1.5	f	113.6	f
∠O1-S-O1'	101.3±1	103.7(4)	112.8	104.0(10)
∠O2-S-O2'	123.3±1	118.3(4)	110.1	118.6(10)
∠O1-S-O2	108.6±0.5	110.6(3)	108.0	110.5(10)
∠O1-S-O2'	106.4±0.5	106.3(3)	109.0	105.9(10)
τ(H-O1-S-O1')[g]	90.9±1	f	84.1	f
τ(H-O1-S-O2)[g]	-20.8±1	f	-36.5	f

a. Bond lengths in angstroms. Bond angles in degrees.

b. Preferred microwave structural parameters and uncertainties from reference 35.

c. X-ray diffraction geometry with estimated standard deviations (esd's) in parentheses from reference 36.

d. Neutron-diffraction 10°K structure from reference 37. The estimated uncertainties are reported in the paper as ±0.05 0.10 Å.

e. X-ray diffraction geometry with esd's in parentheses from reference 38.

f. The hydrogens were not located in either X-ray diffraction study

g. τ(ijkl) is the torsional angle between the ijk and jkl planes.

significant changes are attributed to the hydrogen bond formation in the crystal.[7] I have been able to reproduce these structural changes with the point charge model.

The remainder of this chapter will deal with the results I have obtained for both the gas and solid phases of sulfuric acid. The gas phase will be discussed first, followed by the crystal phase.

GAS

Although vapor pressure studies in 1923 showed that solutions with concentrations exceeding 85% had measurable vapor pressures above 200° F, early studies of gaseous sulfuric acid were hampered by several problems. An infrared (IR) spectrum of gaseous sulfuric acid was not completed until 1965, because of its low volatility and attack on windows at high temperatures. In that study, the observed H_2SO_4 bands were assigned in agreement with the expected chemical series (X-SO_2-Y: X,Y= F, OH, Cl, ...,CH_3). Based on those assignments, the researchers incorrectly concluded that free H_2SO_4 molecules had an approximate tetrahedral configuration with C_{2v} symmetry similar to the other X-SO_2-Y compounds.[39]

The first molecular orbital calculation of the gas phase structure of H_2SO_4 was undertaken in 1978. The purpose of that study was to gain insight into the gas phase reaction of SO_3 and H_2O to form H_2SO_4 using semi-empirical CNDO/2 calculations. Those researchers incorrectly calculated the symmetry of H_2SO_4 as C_{2v} in agreement with the earlier IR study. The calculated structural parameters were O1-H= 1.04 Å, S-O1= 1.63 Å, S-O2= 1.56 Å, $\angle$O1-S-O1'= 97°, $\angle$H-O1-S= 97.5°, and $\angle$O2-S-O2'= 116° with the H-O1-S-O1'-H' atoms being planar.[40] Their configuration is referred to as the compact C_{2v} geometry where the OH

groups point toward and bisect the terminal SO_2 group with a torsional angle ($\angle$H-O1-S-O1' and $\angle$H'-O1'-S-O1) of 180°.

The first ab initio calculation on H_2SO_4 was completed in 1980 due to the importance of sulfur-oxygen compounds in air pollution chemistry, specifically "acid" rain.[41] The optimum geometries in that study were calculated using the STO-3G* basis set. Previous calculations on similar compounds using the STO-3G or 4-31G basis sets had shown poor agreement between experiment and calculated structural parameters though the STO-3G* basis set had been shown to give acceptable geometries. Since the researcher's principal interest was in the geometry about the sulfur atom, the OH length and SOH angle were fixed at 0.994 Å and 105°, respectively [these values corresponded to their optimum values in $SO_2(OH)$]. The calculated STO-3G* geometry for sulfuric acid was S-O1= 1.63 Å, S-O2=1.45 Å, $\angle$O1-S-O1'= 99°, $\angle$O1-S-O2= 107°, and $\angle$O2-S-O2'= 125°. The H-O-S-O dihedral angles were set to 90° by the researchers based upon the best idealized conformation. The addition of d functions to the basis set was shown to greatly improve the calculated energy. The energies calculated at the optimum geometry for the STO-3G* and 4-31G* basis sets showed an energy improvement of 316.1 and 170.6 kcal/mole, respectively, over the energies at the STO-3G and 4-31G levels.[41]

The correct C_2 symmetry was finally determined in 1980 from the microwave spectra of four isotopic species of H_2SO_4. From those spectra, the researchers determined a detailed structure for gaseous H_2SO_4 which is shown in Table 3-1. In contrast to the previously determined compact C_{2v} geometry, the OH bonds were found to have rotated past the SO2 and SO2' bonds resulting in

dihedral angles of -20.8° with them. That structure possessed a H-O1-S-O1'
dihedral angle of 90.9° as compared to 180° found in the CNDO/2 calculation.[35]
The H_2SO_4 molecule with C_2 symmetry is shown in Figure 3-1.

The continued interest in H_2SO_4 prompted two additional ab initio studies
of its structure and torsional modes.[42,43] Both of these studies determined the
potential energy surface for H_2SO_4 as a function of ϕ ($\angle$H-O1-S-O1') and ϕ' ($\angle$
H'-O1'-S-O1). The p,p structure ("p" denotes periplanar or cis) is shown in
Figure 3-2 where $\phi=\phi'=0°$. These researchers performed most of their calculations
at the STO-3G level except for some selected conformations which were calculated
at the 4-31G level. Despite the different structures used for sulfuric acid, as
discussed below, the results of these two studies were surprisingly similar.

The first study was started prior to the completion of the microwave study.
As a result, Kaliannan and coworkers used the geometry of dimethyl sulfate
$[SO_2(OCH_3)]$ obtained by electron diffraction in their study of sulfuric acid. The
O-H bond length and H-O-S bond angle were set at 0.96 Å and 109.47°,
respectively. Their construction of the potential energy surface consisted of
calculations at 22 conformations of ϕ and ϕ'. They found the global minimum
occurring at $\phi=\phi'=90°$ in good agreement with the microwave study value of
$\phi=\phi'=90.9°$. Their calculated dipole moment at that conformation was 2.51 debye
(D) compared to the microwave value of 2.725 D. A secondary minimum was
found to occur at $\phi=-\phi'=120°$ with an energy about 1.2 kcal/mole above the global
minimum. They also determined that the variation in energy was very small in the
range 90°-120° for both ϕ and ϕ', suggesting that the molecule is reasonably flexible
in that range. A comparison of their potential energy surface to that of $H_2PO_4^-$

Figure 3-2

H_2SO_4 p,p structure $\phi=\phi'=0°$ ("p" denotes periplanar or cis)
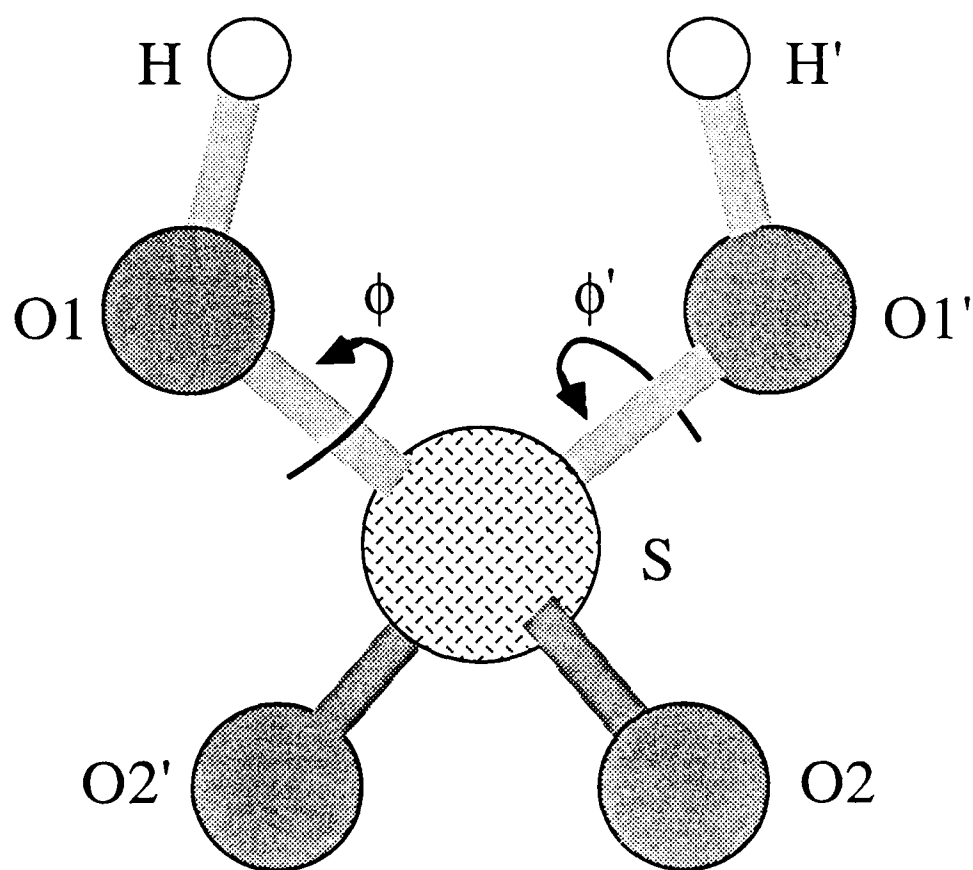
found the two to be very similar with the global minimum occurring at $\phi=\phi'=90°$ in both cases. The results of their 4-31G calculations at the STO-3G optimized geometries confirmed the presence of the global minimum at $\phi=\phi'=90°$ in agreement with the microwave experiment.[42]

Lohr has also conducted a study of the structure and torsional modes of H_2SO_4. In his study, the microwave values for bond lengths and bond angles were used. He constructed his potential surface from 43 calculated points at the STO-3G level. Lohr found the global minimum had C_2 symmetry and occurred at $\phi=\phi'=98.6°$, somewhat larger than the microwave value of $\phi=\phi'=90.9°$. A local minimum with C_s symmetry was also found at $\phi=-\phi'=104°$ with an energy of 1.36 kcal/mole relative to the global minimum. Calculations at eleven selected points were done using the larger 4-31G basis set. The structure with C_2 symmetry was found to have a minimum energy at $\phi=\phi'=94.9°$ which is somewhat closer to the microwave value than is the STO-3G value.[43] The results of both torsional mode studies confirm the C_2 symmetry which is observed in the microwave study.

I optimized the gas phase of sulfuric acid with several different basis sets. The programs TEXAS, TEXAS(D), and GAUSSIAN-82 [44] were used to obtain an optimum structure at the 6-31G** level. In addition, calculations were conducted at the 4-31G** level using TEXAS and at the STO-3G* level using GAUSSIAN-85 [45]. The results of my calculations on gaseous sulfuric acid are presented in Table 3-2.

The 6-31G** basis set admirably reproduces the experimental structure. With very few exceptions, the calculated 6-31G** structure is within the experimental uncertainties of the microwave study. The major variances occur in

Table 3-2[a]

Sulfuric Acid (H_2SO_4) Gas Phase Geometries

	MW[b]	6-31G**[c]	6-31G**[c]	6-31G**[c]	4-31G**[c]	STO-3G*[c]
			TEXAS(D)	G-82		G-85
S-O1	1.574±0.01	1.570	1.569	1.569	1.563	1.620
S=O2	1.422±0.01	1.411	1.411	1.411	1.408	1.446
O1-H	0.97±0.01	0.950	0.950	0.950	0.950	0.993
∠H-O1-S	108.5±1.5	110.7	110.8	110.8	111.2	105.6
∠O1-S-O1'	101.3±1	101.8	101.8	101.8	101.7	100.1
∠O2-S-O2'	123.3±1	123.5	123.6	123.6	123.5	125.6
∠O1-S-O2	108.6±0.5	108.1	108.1	108.1	108.3	108.9
∠O1-S-O2'	106.4±0.5	106.7	106.7	106.6	106.5	105.2
τ(H-O1-S-O1')	90.9±1	88.9	89.2	88.8	87.8	79.1
τ(H-O1-S-O2)	-20.8±1	-23.2	-22.9	-23.3	-24.2	-31.0

Energy:

Hartree		-698.051422		-698.052804		-689.766048
			-698.052805		-697.659157	
kcal/mole		-438,033.781		-438,034.65		-432,834.63
			-438,034.649		-437,787.631	

a. Bond lengths in angstroms. Bond angles in degrees.

b. Preferred microwave structural parameters and uncertainties from reference 35.

c. This work. Calculations run with TEXAS unless noted otherwise.

the torsional angles which are notoriously difficult to reproduce. Considering the ± 2.0° uncertainty in the value of the calculated torsion angles, the agreement is very good.

The development of TEXAS(D) by Pulay's group prompted me to optimize the gas phase structure with it for comparison. As shown in Table 3-2, the 6-31G** structures are identical for both TEXAS and TEXAS(D). My calculations confirm that the displaced p functions used to construct d functions in TEXAS are more than adequate. The only difference between these two calculated structures is in the energy. The TEXAS(D) energy is 0.868 kcal/mole lower than that calculated in TEXAS. The improved energy in TEXAS(D) must be due to the use of true d functions. For most calculations, this energy difference is insignificant. Based on calculated structures and energy, neither TEXAS nor TEXAS(D) offer any advantage over the other with the exception of the slightly lower energy in TEXAS(D). In terms of computation time, TEXAS(D) is superior, posting decreases of up to 30% over TEXAS. TEXAS(D), however, requires double the amount of disk space to store the integrals as compared to TEXAS.

Because of the recent acquisition of a Cray version of GAUSSIAN-82, I decided to make a comparison between it and TEXAS(D). Since both programs incorporate true d functions, I expected identical results. As shown in Table 3-2, the results are essentially identical. The few tenths of a degree difference between torsional angles is well within the calculated uncertainty of ± 2.0°. The TEXAS(D) program calculated an energy which is only 6×10^{-4} kcal/mole lower than GAUSSIAN-82. Based upon my comparison, both TEXAS(D) and GAUSSIAN-82 do give identical results for calculations conducted with the same basis set.

Initially, I was interested in reducing the computation time required for one optimization run. As a result, I completed an optimization run of gaseous sulfuric acid at the 4-31G** level. The 4-31G** basis set I utilized contained a 4-31G** basis on sulfur and 6-31G** on both oxygen and hydrogen. As shown in Table 3-2, the 4-31G** basis set gave structural parameters almost identical to those computed with TEXAS at the 6-31G** level. The major distinctions are the shorter O1-S bond length and the torsional angles at the 4-31G** level. The computation time saved at the 4-31G** level was significant. The 4-31G** calculation ran 15% faster than the 6-31G** calculation, 1761 seconds compared to 2066 seconds. The time savings is due to the reduction in the number of primitive Gaussian functions. Although the number of contracted Gaussians is the same for both basis sets at 89, the number of primitive Gaussians is reduced from 208 to 198 in going from the 6-31G** basis set to the 4-31G** basis set. The major disagreement between the two calculations is the total energy. The 6-31G** calculation results in an energy 247 kcal/mole lower than the energy at the 4-31G** level. For many calculations, the 4-31G** basis set would be satisfactory. Since I was concerned with observing structural changes, I chose to use the more accurate 6-31G** basis set in the crystal calculations. In addition, the 6-31G** basis set {(11s4p1d/4s1p) contracted to [4s2p1d/2s1p]} represents a significant improvement over the basis set used by Saebø and coworkers {(7s3p/4s) [4s2p/2s]}. The 6-31G** basis set not only increases the number of primitive functions but also adds polarization functions to hydrogen and the heavy atoms.

In order to make comparisons with some dimer calculations, I optimized sulfuric acid at the STO-3G* level. As shown in Table 3-2, the calculated

parameters at this level differ greatly from the experimental structure. The large

error in the torsional angles at the STO-3G* level confirms the need for polarization

functions on oxygen to accurately calculate these angles. More importantly, while

no symmetry restrictions were placed on any of the other calculations, I had to

restrict the STO-3G* calculation to C_2 in order to prevent the program from

determining a structure with C_1 symmetry. While minimal basis set calculations

can yield valuable information, the need for accurate structural information almost

always requires using a larger basis set.

CRYSTAL

The first X-ray diffraction study of sulfuric acid was completed in 1954 by

Pascard. That study incorrectly concluded that sulfuric acid crystallized in the

noncentrosymmetric space group C2 and possessed C_{2v} symmetry.[46] In 1964,

Pascard-Billy refined the original intensity data with anisotropic temperature factors

for oxygen atoms to a reliability (R) factor of only 0.124. The reported dimensions

of the H_2SO_4 molecule deviated significantly from idealized C_{2v} symmetry.

Pascard-Billy determined that the correct space group was actually C2/c and the

H_2SO_4 molecule possessed C_2 symmetry. Although Pascard was not able to locate

the hydrogens, he theorized that they each formed a hydrogen bond with a double

bonded oxygen on an adjacent molecule. In that configuration, one H_2SO_4

molecule is hydrogen bonded to four adjacent molecules with the hydrogen atom

lying on the -O1...O2= line.[38]

In 1978, Yu and Mak felt that the atomic parameters reported earlier could

be further refined by full-matrix anisotropic least squares with correction for

secondary extinction. Their study showed significant improvement of the standard

deviations in atomic parameters over those reported earlier with an R value of 0.099. Their measured hydrogen bond length (O1-H...O2) of 2.624 Å belongs to the short type. They concluded that the hydrogen atom almost lay on the internuclear O1...O2 line if a tetrahedral S-O-H angle was assumed.[36]

The hydrogen atoms were finally located in 1983 by Moodenbaugh and coworkers using powder neutron-diffraction techniques. Diffraction data was collected near the melting point (240°K) and at 10°K to search for order-disorder transitions in the hydrogen bond network. The neutron-diffraction scans revealed, to the limits of detection, that the sulfuric acid sample was single phase with monoclinic symmetry at both temperatures. The principal conclusions from their study were that the hydrogens were ordered at both temperatures and the parameters of the other atoms were qualitatively consistent with the single-crystal X-ray studies.[37]

The generation of the point charges used in my calculations was facilitated by the use of several computer programs. The BMFIT[47] (Best Molecular Fit) program derives the best least-squares fit between two sets of atoms. I used BMFIT in order to convert calculated structures into fractional coordinates in the crystal space. The program DAESD[48] calculates interatomic distances and angles in crystal structures. The DAESD program was used to generate all the molecules within a given unit cell. The programs ZERO and MOLE were written by me in order to generate the actual point charge locations. Both programs convert the contents of a unit cell into a molecule and its nearest neighbors. In the program ZERO, all neighbor atoms within a given sphere of radius r from the central molecule are punched. In addition, a dummy charge is generated and placed at

(100,100,100) in order to maintain the neutrality of the point charges. In MOLE, all neighbor molecules that have their central atom within r from the central molecule are punched. In the case of MOLE, the neutrality of charge is maintained by including whole molecules instead of individual atoms.

My studies have shown that great care must be taken in generating the point charges. As discussed in Chapter Two, I initially tried to limit the number of point charges in order to reduce the computation time. I did this by using the program ZERO to generate the point charges. The program ZERO allowed me to include only the nearest atoms and not the nearest molecules. I could then eliminate atoms on adjacent molecules that were far enough away that they had essentially zero electrostatic interactions with the central molecule. However, this method proved to be entirely unsatisfactory. Not only was the savings in computation time negligible, but this method also introduced artificial symmetries into the calculated structure. In my particular case, the point charges generated using the program ZERO artificially reduced the symmetry of H_2SO_4 from C_2 to C_1. As a result, all of my crystal calculations were made using the nearest neighbor molecules generated by MOLE. After careful scrutiny of the point charges, I found that including the 18 nearest H_2SO_4 molecules insured that all nearest neighbor atoms were included in the point charges. All of the reported calculated crystal structures used 126 point charges based on the 18 nearest H_2SO_4 molecules.

The crystal calculations which I have completed can be divided into four categories - SF, SE, MF, and IF. These designations are used throughout the remainder of the paper and are defined as follows:

SF-   A single optimization cycle was run. (Note: An optimization cycle means that the convergence criteria of Chapter Two have been met.) The point charge magnitudes are based on the optimized free (gas phase) molecule. The point charge locations are based on the experimental crystal structures. This is the method used by Saebo and coworkers.

SE-   This is identical to the SF method except that the point charge magnitudes are based on a calculation at the experimental crystal geometry.

MF-   This method is a continuation of the SF method involving multiple optimization cycles. In this case, a Mulliken population analysis is run on the new "free" molecule geometry obtained from the SF method. (Note: The term "free", in quotation marks, refers to the central molecule surrounded by the point charges.) The new net charges are assigned to the experimental point charge locations and another optimization cycle is completed on the "free" molecule. The process is repeated until the "free" molecule converges in both structure and energy.

IF-   This is an iterative method involving multiple optimization cycles similar to the MF method. In this case, however, both the point charge magnitudes and locations are based on the optimized free (gas phase) molecule. The only information used from the experimental crystal study is the unit cell dimensions and space group. After each optimization cycle, the magnitude and location of

the point charges are adjusted to those corresponding to the newly optimized "free" molecule. The process is continued until the "free" molecule converges in both structure and energy.

The SE method was conceived by me to test the sensitivity of the calculated crystal structures to the magnitude of the point charges. A Mulliken population analysis was run on the wave function from a single point SCF calculation at the experimental geometry to obtain the experimental net charges. As expected, the net charges from the experimental geometry differed significantly from those of the optimized free molecule. Although using the net charges from the free molecule seems logical since a wave function already exists, no study has been made previously to compare the effects of the two sets of net charges. Since a single point SCF calculation is relatively small (about 650 seconds), the calculation of the experimental net charges and their subsequent use in the SE method seems a reasonable alternative to the SF method.

The use of the iterative method in the point charge model is an extension of an improvement proposed by Saebø and coworkers. They simply suggested that the point charge model might be improved by including the net charges of the newly optimized "free" molecule. My idea was to iterate this process until the molecule converged in both structure and energy. My iterative technique is therefore self-consistent. The major advantage of my method is that it adds flexibility to the point charge model. A significant concern with the point charge model is that it may not incorporate all the forces which bind crystals together. As discussed in Chapter Two, all of the binding forces in crystals involve charged particle interactions. Since the model basically allows for electrostatic interactions

between the electrons and the point charges, the iterative method should accurately recreate the environment inside the crystal. In addition, any effect of the arbitrary assignment of net charge in the population analysis should be greatly minimized since the net charges are varied in response to their environment.

I devised the IF method for a couple of reasons. First, experimental crystal data is often incomplete or inaccurate. As discussed previously, X-ray crystallography frequently cannot locate hydrogen atoms. Even when all the atoms are located, the precision with which an atom can be positioned in a crystal is subject to systematic errors. These errors can be divided into two classes: errors in the model and errors in the data. If it was possible to collect data with no errors, many significant structural errors could be introduced if an improper model is used in the refinement. The IF method is not as dependent on the experimental data since it uses only the cell dimensions and space group of the crystal. The cell dimensions and space group are more easily determined and can be found even if all the atoms are not located. Second, a principal concern with the point charge model is that it may not adequately represent the crystal environment. The IF method allows for movement of the point charges. Therefore, the point charges should ultimately reside in the crystal locations if the point charges properly model the crystal environment. Thus, the IF method serves as a test of the validity of the point charge model.

The first calculations that I completed were based on the X-ray study of Yu and Mak. Since the hydrogens were not located in their study, I assigned their location by assuming an O1-H bond length of 0.95 Å and a hydrogen bond angle ($\angle$O1-H...O2) of 180°. The results of these calculations are presented in Table 3-3.

In addition to the calculations based on the X-ray study, I also conducted calculations based on the neutron-diffraction study. The 10°K neutron-diffraction data was used as the basis for the calculations because of its minimal thermal motion and due to errors in the 240°K data I discovered. The results of these calculations are presented in Table 3-4. The numerous problems with the neutron-diffraction study will be discussed later.

One aspect that all of the calculated solid structures share is a lower energy than the gas phase. The energy improvement in the solid structures is on the order of 50-70 kcal/mole. The lower energy in the crystal is expected based on the stabilizing effect of the neighbor molecules in the solid. The calculated energy improvement which corresponds to 12.5-17.5 kcal/mole per hydrogen bond compares favorably to 7.8 kcal/mole for cyanoformamide[9], 5.4 and 5.9 kcal/mole for $CH_3CN...HOCH_3$, respectively[49], 3.9-9.6 kcal/mole for the water dimer (depending upon basis set)[50], and 7.0-10.3 kcal/mole for the various monohydrated formamide complexes[51]. In addition, all of the calculated crystal structures mimic the major structural changes which occur in H_2SO_4 in going from a gas to a solid. Specifically, the calculated crystal structures show a substantial shortening of the S-O bond along with an increase in the $\angle O1$-S-$O1'$ and a decrease in the $\angle O2$-S-$O2'$ compared to the gas. Further, all of the calculated crystal structures agree with the general and very characteristic structural feature between bond angles for sulphones (XSO_2Y). Hargittai has demonstrated that the $\angle$ X-S-Y $<$ $\angle$ X(Y)-S=O $<$ $\angle$ O=S=O, regardless of the X and Y ligands. The $\angle$ O=S=O is considerably larger than the ideal tetrahedral angle while the $\angle$ X-S-Y is considerably smaller.[52] While these results alone substantiate the point charge

Table 3-3[a]

Sulfuric Acid (H_2SO_4) X-ray Crystal Geometry

	XRAY(1978)[b]	SF[c]	SE[c]	MF[c]	IF[c]
S-O1	1.528(5)	1.558	1.557	1.553	1.552
S=O2	1.419(5)	1.422	1.424	1.428	1.428
O1-H	0.950[d]	0.971	0.972	0.978	0.978
O1...O2[e]	2.624(8)	2.553	2.553	2.550	2.556
∠H-O1-S	109.9[d]	113.9	114.1	114.7	114.8
∠O1-S-O1'	103.7(4)	104.3	104.6	105.3	105.2
∠O2-S-O2'	118.3(4)	120.8	120.5	119.6	119.4
∠O1-S-O2	110.6(3)	107.3	107.3	107.2	107.4
∠O1-S-O2'	106.3(3)	108.0	108.1	108.4	108.3
∠S-O1...O2[e]	110.0(3)	111.3	111.3	111.3	111.1
∠O1...O2[e]-S[e]	157.9(4)	160.7	160.7	160.5	160.4
τ(H-O1-S-O1')	86.3[d]	92.3	92.0	91.6	89.5
τ(H-O1-S-O2)	-27.3[d]	-22.2	-22.6	-23.7	-25.7

Energy:

Hartree	-698.130620	-698.155672
	-698.134681	-698.161332
kcal/mole	-438,083.479	-438,099.199
	-438,086.027	-438,102.750

a. Bond lengths in angstroms. Bond angles in degrees.

b. X-ray diffraction geometry with esd's in parentheses from reference 36.

c. This work. Calculated using the 6-31G** basis set.

d. Based on setting the O1-H bond length to 0.95 Å and the O1-H...O2 bond angle to 180°.

e. Atom is located at fractional coordinates -1/2+x,1/2+y,z on an adjacent molecule.

Table 3-4[a]

Sulfuric Acid (H_2SO_4) Neutron-Diffraction 10°K Geometry

	ND[b]	SF[c]	SE[c]	MF[c]	IF[c]
S-O1	1.48	1.554	1.551	1.549	1.552
S=O2	1.49	1.425	1.428	1.431	1.428
O1-H	0.91	0.972	0.976	0.980	0.979
O1...O2[d]	2.52	2.55	2.55	2.55	2.55
H...O2[d]	1.65	1.59	1.58	1.58	1.58
∠H-O1-S	113.6	113.5	114.4	114.3	115.2
∠O1-S-O1'	112.8	104.9	105.7	106.0	105.4
∠O2-S-O2'	110.1	120.0	119.1	118.6	119.5
∠O1-S-O2	108.0	107.2	107.2	107.0	107.3
∠O1-S-O2'	109.0	108.3	108.4	108.8	108.2
∠O1-H...O2[d]	175	171.5	173.8	171.3	172.7
∠S-O1...O2[d]	111.9	112.1	112.0	112.1	112.3
∠O1...O2[d]-S[d]	155.3	159.3	159.1	159.1	158.9
τ(H-O1-S-O1')	84.1	93.1	90.5	92.6	91.3
τ(H-O1-S-O2)	-36.5	-21.9	-25.1	-23.4	-23.9

Energy:

Hartree		-698.136173	-698.165534	
			-698.160937	-698.160931
kcal/mole		-438,086.963	-438,105.387	
			-438,102.503	-438,102.499

a. Bond lengths in angstroms. Bond angles in degrees.

b. Neutron diffraction 10°K structure from reference 37. The estimated
uncertainties are reported in the paper as ±0.05-0.10 Å.

c. This work. Calculated using the 6-31G** basis set.

d. Atom is located at fractional coordinates -1/2+x,1/2+y,z on an adjacent
molecule.

model, the remaining differences between the calculated and experimental crystal structures need closer scrutiny.

The differences between the calculated and neutron-diffraction crystal structures are easily explained by examining the experimental data. Moodenbaugh and coworkers report estimated standard deviations (esd's) of ± 0.05-0.10 Å. Although their calculated esd's are about 0.01 Å, the larger esd's arise from an apparent discrepancy in the O1-H bond length which is known to be temperature independent to about ± 0.002 Å.[37] Based on their ± 0.05-0.10 Å uncertainty in bond lengths, all of the calculated values fall within that range. Any comparison with the neutron-diffraction study by Moodenbaugh and coworkers is essentially useless because of the extremely large uncertainties in the experimental data.

There are numerous reasons for the large errors reported by Moodenbaugh and coworkers. First, the structural model that is used in any refinement of the raw crystal data is crucial to the results. In their study, they based the heavy atom positions on the 1965 X-ray study with its larger esd's instead of the 1978 study with its smaller esd's. They were unaware of the 1978 study. They also chose to use isotropic temperature factors for simplicity, even though both of the X-ray diffraction studies indicate that anisotropic factors would be more appropriate. Their R factors, on the order of 0.20, are approximately double those from the X-ray diffraction studies. Second, the quality of their data is rather poor with an unfavorable typical peak to background ratio of 1:2. This is probably due to the fact that they used a powder sample since they could not obtain a suitable single crystal. The high background caused by incoherent scattering required them to use the Rietveld refinement method which is not normally used.

Finally, the data from the neutron-diffraction experiment is questionable at
best. Table 3-5 shows the bond lengths and angles reported by them at 240°K.
However, when I used their coordinates to calculate structural parameters, the
actual S-O1 bond length differs greatly from that they reported. At first glance,
only the reported S-O1 bond length would appear to be in error. If the value of
1.67 Å that I calculated is correct, the S-O1 bond length would undergo a
shortening of 0.19 Å between 240°K and 10°K which is highly unlikely since
H_2SO_4 was found to be ordered at both temperatures. In addition, the values I
calculate from their data for the $\angle O1$-S-O1' (=87.9°) and $\angle O2$-S-O2' (=133.1°)
differ greatly from those in the X-ray diffraction study (103.7° and 118.3°) and in
the neutron-diffraction study at 10°K (112.8° and 110.1°). The discrepancies in the
S-O1 bond length and the angles about sulfur suggest to me that there is an error in
the fractional coordinates of the sulfur atom. Since sulfur occupies the special
position 0,y,1/4, the error appears to be in the y fractional coordinate. I have made
several attempts to determine the correct sulfur coordinates by varying the y
coordinate. In my opinion, the most probable structure for H_2SO_4, based on the
data presented in the paper at 240°K, occurs when y=0.068 as shown in Table 3-5.
The reported value is y=0.028(6). My value of 0.068 appears to be a logical
transposition of the reported value. At y=0.068, there is much better agreement
between the 10°K and 240°K structures. I have talked to Moodenbaugh about this
problem. Moodenbaugh was not previously aware of the problem and told me he
put much more reliance on the heavy atom positions from the X-ray studies.
Further, he indicated absolutely no interest in trying to resolve the problem. The
numerous problems with the neutron-diffraction study by Moodenbaugh and

Table 3-5[a]

H$_2$SO$_4$ Neutron-Diffraction Structural Parameters at 240°K

	Reported[b]	Calculated	Probable
S-O1	1.54	1.67	1.54
S=O2	1.40	1.40	1.49
O1-H	1.00	1.00	1.00
O1...O2[c]	2.47	2.47	2.47
H...O2[c]	1.49	1.50	1.50
∠O1-H...O2[c]	163	164	164
∠O1-S-O1'		87.9	97.9
∠O2-S-O2'		133.1	119.6

a. Bond lengths in angstroms. Bond angles in degrees.

b. Neutron diffraction 10°K structure from reference 37. The estimated
uncertainties are reported in the paper as ±0.05-0.10 Å.

c. Atom is located at fractional coordinates -1/2+x,1/2+y,z on an adjacent
molecule.

coworkers certainly warrant another neutron-diffraction study of H_2SO_4.

A comparison of the calculated and X-ray crystal structures in Table 3-3 shows relatively good agreement. By far the largest discrepancy is in the S-O1 single bond length. The X-ray experiment determined the S-O1 distance to be about 0.03 Å shorter than the calculation. As discussed earlier, a major disadvantage of X-ray diffraction is that it determines distances between centers of electron density and not nuclei. Since the shorter bond length could be a consequence of the X-ray experiment, I decided to investigate it further. In order to investigate the S-O1 bond length discrepancy, I chose three distinct approaches. The first was to calculate the crystal structure with an expanded basis set. The second involved calculations on the H_2SO_4 dimer. In the third method, I used the program MOCALC[53] in order to look at the total electron density along the S-O1 bond.

Since the point charge model may not adequately describe the hydrogen bonding, the calculated S-O1 bond length may be too long. However, various studies on dimers have shown that not only similar double zeta basis sets[49,51,54,55] but also even the minimal STO-3G basis set[50] adequately describe hydrogen bonding. Saebø and coworkers concluded from their study of cyanoformamide that hydrogen bonding was dominated by electrostatic effects.[9] In addition, Tang and Fu concluded from ab initio studies of hydrogen bonding between methyl cyanide (CH_3CN) or methyl isocyanide (CH_3NC) and methanol (CH_3OH) that it was a result of ionic binding of two closed-shell systems.[49] Nevertheless, in order to see if an expansion in the basis set might better describe the hydrogen bonding, a calculation was made with the 6-31 +G** basis set.[10] The "+" implies the addition

of a diffuse sp shell to the hydrogen atoms (exponent=0.0360). The addition of diffuse functions is required in the calculation of anions, transition structures, and other species with significant electron density far removed from the nuclear center. The optimized geometry with the 6-31 +G** basis set was practically identical to that of the 6-31G** basis set with no difference in the S-O1 bond length.

Another approach I pursued was to optimize the structure of the H_2SO_4 dimer. The two molecules chosen were those that were hydrogen bonded in the crystal. The dimer calculation showed a definite shortening of the S-O1 bond at the STO-3G* level. The hydrogen bonded S-O1 and S-O2 bond lengths were 1.58 Å and 1.46 Å, respectively, compared to 1.62 Å and 1.45 Å in the monomer at the STO-3G* level. The shortening shown in the dimer must be viewed with caution. In the optimized dimer, the two molecules rotated, as a result of the program, such that two hydrogen bonds were formed between them instead of only one as found in the crystal. This is apparently caused by the lack of neighbor molecules which prevent the rotation in the crystal. My attempts to conduct dimer calculations at the 6-31G** level with the inclusion of the point charges have not been successful. I initially planned to optimize the dimer structure at the STO-3G* level with the inclusion of the point charges. However, because of the success of the total electron density plot in explaining the shortened bond in the X-ray study, I have not completed any additional dimer calculations.

The program MOCALC[53] allows plotting electron density of either a single molecular orbital or all of the molecular orbitals. MOCALC was specifically written to use the data generated in the TEXAS program. In order to investigate the shortened S-O1 bond, I have completed a total electron density plot of H_2SO_4 in

the O1-S-O1' plane which is shown in Figure 3-3. As Figure 3-3 clearly shows, the electron density of the O1 atom is definitely shifted toward the S atom. After talking with several crystallographers, I have determined that there is no commonly used quantitative method to account for this apparent bond shortening. The crystallographers simply accept the fact that it exists. In order to get a quantitative feel for the magnitude of this shortening, I have simply assumed the location of the center of the electron density on the O1 atom in Figure 3-3. By making simple measurements with a ruler, I have determined, that in the case of H_2SO_4, the shortening of the S-O1 bond length in the X-ray study is on the order of 0.03-0.05 Å. Thus, as shown in Figure 3-3, I conclude that the short S-O1 bond length reported in the X-ray studies is a consequence of the X-ray experiment.

The various methods used in this study to determine the magnitude and location of the point charges yielded some interesting results. As shown in Table 3-3 and 3-4, the SF and SE methods yielded almost identical geometries despite the differences in the magnitude of the point charges. In both cases, the magnitude of the point charges obtained from the experimental crystal structures in the SE method differed by as much as 15% from those calculated for the optimized free molecule. The differences between the SF and SE structures were no more than 0.004 Å in bond lengths and 0.9° in bond angles. In most cases, within the uncertainties of the calculations, the two methods gave structures which agree. The convincing agreement between these two methods shows that the structures calculated using the point charge method are relatively insensitive to the magnitude of the charges. This indicates that the arbitrary manner in which the Mulliken population analysis assigns net charge has little effect on the calculated results.

Figure 3-3

Total Electron Density Plot of H_2SO_4 in the O1-S-O1' Plane

CONTOUR INTERVAL —0.060000
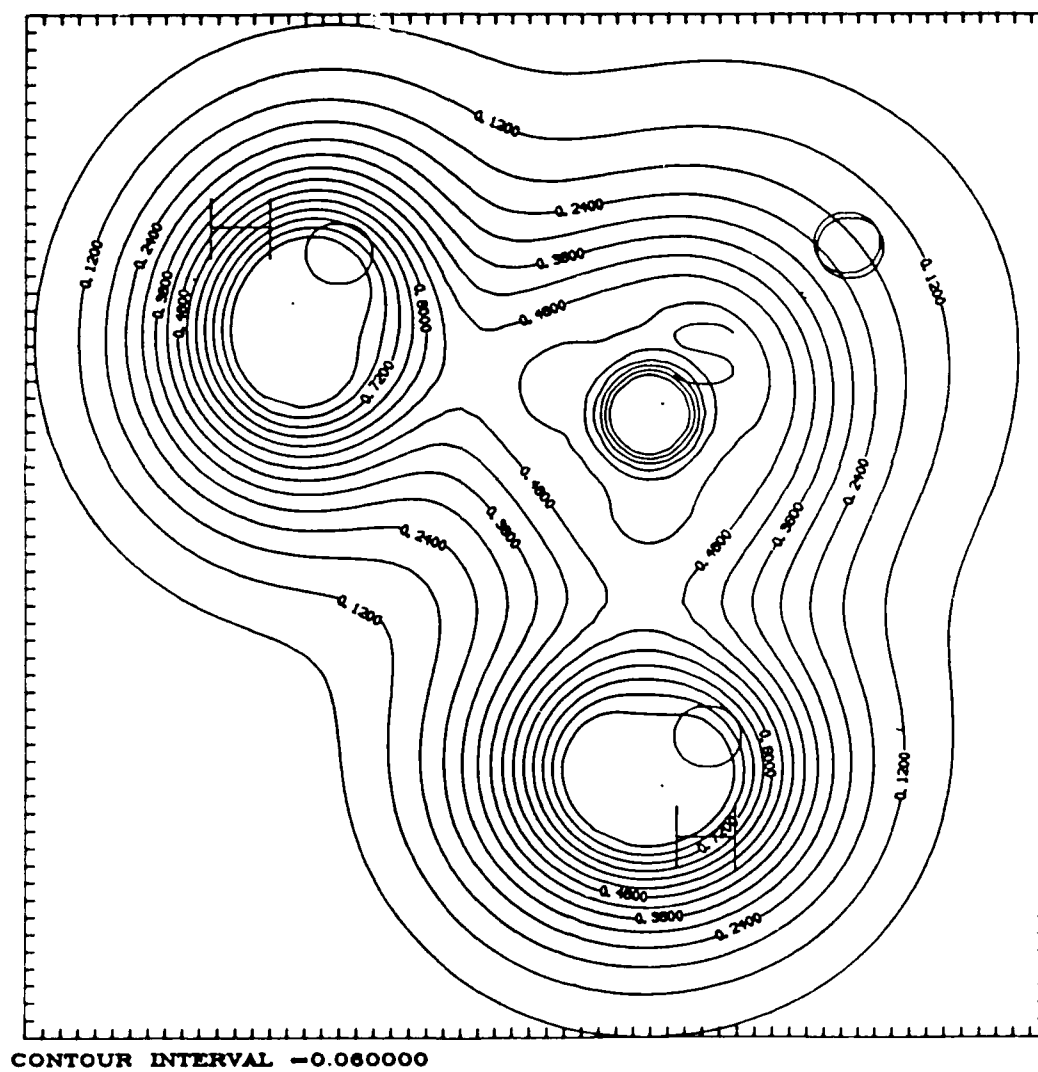
My study shows that the iterative technique used in the MF and IF methods offers several advantages over the single optimization cycle methods. Both of these methods show substantial improvements in the total energy over the SF method. The energy improvements are on the order of 15-19 kcal/mole. Throughout the MF and IF optimization cycles, the calculated structural parameters continued to better approximate those in the crystal. Specifically, the S-O1 bond length continued to shorten, the $\angle$O1-S-O1' increased, and the $\angle$O2-S-O2' decreased. The improvements in both the energy and structural parameters confirm the use of the iterative approach. One particularly interesting result from the MF and IF methods is the change in gross atomic populations. Three ab initio studies by Ottersen and Jensen found that there is a transfer of electron density from the hydrogen atom to the acceptor atom. The formamide ($HCONH_2$) dimer showed a transfer of 0.05 electron across the hydrogen bond.[54] Ottersen's study of the keto ($HCONH_2$) and enol (HOCHNH) tautomers of formamide exhibited gross atomic population increases of 0.057 and 0.089 on the acceptor atoms and decreases of 0.046 and 0.044, respectively, in the bridging hydrogens.[55] Their study of the four monohydrated formamide complexes demonstrated gross atomic population increases of 0.009-0.034 for the acceptor atoms and decreases of 0.015-0.039 for the bridging hydrogens.[51] The gross atomic populations for my calculations using the iterative method are presented in Table 3-6. All four of my calculations clearly follow the trend of Ottersen and Jensen by exhibiting a transfer of electron density from the bridging hydrogens to the acceptor atoms (O2/O2'). These results confirm the ability of the point charge model to accurately describe the crystal environment for hydrogen bonded systems. In summary, the iterative technique

Table 3-6[a]

H$_2$SO$_4$ Gross Atomic Populations

		Free Molecule	Optimized Geometry[b]	Net Change
X-ray:				
MF-	S	14.18843	14.11860	-0.070
	O1/O1'	8.65419	8.67702	+0.023
	H/H'	0.60258	0.51039	-0.092
	O2/O2'	8.64902	8.75329	+0.104
IF-	S	14.18843	14.10879	-0.080
	O1/O1'	8.65419	8.67743	+0.023
	H/H'	0.60258	0.50813	-0.094
	O2/O2'	8.64902	8.76004	+0.111
Neutron-Diffraction:				
MF-	S	14.18843	14.11909	-0.069
	O1/O1'	8.65419	8.66920	+0.015
	H/H'	0.60258	0.50504	-0.098
	O2/O2'	8.64902	8.76621	+0.117
IF-	S	14.18843	14.10930	-0.079
	O1/O1'	8.65419	8.67745	+0.023
	H/H'	0.60258	0.50761	-0.095
	O2/O2'	8.64902	8.76029	+0.111

a. All values were calculated from the Mulliken population analysis with the 6-31G** basis set.

b. These values were obtained using the indicated methods after the calculations converged in both energy and structure. In all cases this required 5 optimization cycles.

tends to minimize any detrimental effects of the Mulliken population analysis. In addition, by allowing the point charge model to dynamically change in relation to its environment, any effects or forces which are not entirely electrostatic by nature appear to be accounted for. The only disadvantage of the iterative technique is the amount of computation time required. With each run averaging 2,500 seconds and up to 30 runs required, the iterative technique is fairly expensive. However, the accurate results from these methods far outweigh their cost. The MF and IF methods are clearly superior to the SF method used by Saebø and coworkers.

My study has shown that the IF method is particularly useful. Not only does it allow calculations on molecules for which incomplete experimental structures exist, but it also gave better results in my calculations based on the X-ray data. The fact that the MF and IF X-ray structures are almost identical substantiates the point charge model. The point charge model reproduces the deformation forces which are present in the solid upon crystallization as shown by the IF method. In the IF method, the point charges are initially positioned in the free molecule geometry but they are subsequently adjusted to the newly calculated "free" molecule geometry. Since the point charges eventually assume the approximate structure of the crystal, the point charge model must essentially reproduce the forces present in the crystal. Based on my results, both the MF and IF methods are superior to the SF method and they allow much more flexibility in the model. Since both the MF and IF methods have been shown to give almost identical results, either method can be used but the IF method should certainly be used in cases where the experimental data is incomplete.

A major concern with the point charge model is the dependence of the

calculated structure on the magnitude of the point charges. In order to investigate

the dependance, I made several runs in which I varied only the magnitude of the

point charges. The point charges were positioned according to the arrangement

found in the 10°K neutron-diffraction study and the free molecule was optimized

inside these point charges as in the SF method. The results of those calculations

are shown in Table 3-7. In run #1 which uses the SE method, the magnitude of the

point charges was calculated from the experimental geometry. The net charges in

run #2 were calculated from the optimized free molecule. Run #2 is equivalent to

the SF results reported in Table 3-4. In run #3, I arbitrarily normalized the net

charges of the free molecule to the O2/O2' net charge. Despite the difference in the

net charges which vary by up to 80%, the calculated geometries are extremely

similar. The maximum difference in bond lengths and bond angles is 0.02 Å and

2.1°, respectively, occurring only in run #3 with its extreme values of charge. I

conclude from these results that the structures calculated using the point charge

model are fairly insensitive to the magnitude of the point charges. Therefore, the

arbitrary assignment of net charge by the Mulliken population analysis has little

effect of the calculated structure.

Table 3-7[a]

Calculated H_2SO_4 Solid Phase Geometries

	#1[b]	#2[b]	#3[b]
Net Charge:			
S	1.75069	1.81157	2.79124
O1/O1'	-0.56293	-0.65419	-1.00796
H/H'	0.39592	0.39742	0.61234
O2/O2'	-0.70833	-0.64902	-1.00000
Structure:			
S-O1	1.551	1.554	1.549
S=O2	1.428	1.425	1.436
O1-H	0.976	0.972	0.992
∠H-O1-S	114.4	113.5	115.6
∠O1-S-O1'	105.7	104.9	106.6
∠O2-S-O2'	119.1	120.0	118.1
∠O1-S-O2	107.2	107.2	106.4
∠O1-S-O2'	108.4	108.3	109.4
τ(H-O1-S-O1')	90.5	93.1	91.1
τ(H-O1-S-O2)	-25.1	-21.9	-25.6
Energy:			
Hartree	-698.160937	-698.136173	-698.194785
kcal/mole	-438,102.503	-438,086.963	-438,123.743

a. Bond lengths in angstroms. Bond angles in degrees.

b. Geometry optimized at the 6-31G** level. The point charge locations are based on the 10°K neutron-diffraction data. The magnitude of the point charges were obtained as explained in the text.

Chapter Four

CONCLUSION

In this paper, I have presented a thorough ab initio study of sulfuric acid and the point charge model. The point charge model has been shown to be extremely advantageous in the calculation of crystal structures with few limitations. In addition, I have presented a comprehensive review of various crystal field simulation methods which have been used. In this chapter, the important results from my study are summarized and my suggestions for future work are offered.

My calculations of the gas phase structure of H_2SO_4 show that the 6-31G** basis set accurately reproduces the microwave structure. With few exceptions, the calculated 6-31G** structure is within the experimental uncertainties of the microwave study. The 4-31G** basis set gave a similar structure to the 6-31G** results with a substantial savings in computation time. My study has confirmed that the use of displaced p functions to simulate d functions has essentially no effect on the calculated structure. The only difference being in the total energy which is less than 1 kcal/mole lower with the true d functions. The ab initio programs TEXAS(D) and Gaussian-82 give identical results with the 6-31G** basis set for H_2SO_4 as expected. My calculations confirm that polarization functions are absolutely essential to reproduce torsional angles on oxygen.

My calculations of the crystal structure of H_2SO_4 demonstrate that the point charge model accurately reproduces the structural trends which occur in transforming from the gas to solid phase. My study of the point charge model proves that it precisely simulates the deformation forces which are present in the

solid upon crystallization. During the course of my study, I discovered that the only neutron-diffraction study of H_2SO_4 is plagued by numerous errors, rendering it totally useless.

The calculated crystal structures based on the X-ray diffraction study are in good agreement with the experiment. The major discrepancy is in the S-O single bond length which is calculated about 0.03 Å longer than in the X-ray study. After a thorough investigation, I conclude that the discrepancy is due to a shifting of electron density from the oxygen atom towards the sulfur atom, resulting in the short experimental bond length.

The iterative technique gives superior results to any of the single optimization cycle methods. Even with the point charges arranged in the gas geometry, the point charge model gives almost identical structural results to those calculations where the charges are positioned in the crystal structure. The point charge model more than adequately describes the crystal forces, especially for systems involving hydrogen bonding.

The iterative technique minimizes any possible drawbacks of the point charge model. Any consequence of the arbitrary assignment of net charge by the Mulliken population analysis is minimized by allowing the charges to vary. By allowing the point charge model to dynamically change in relation to its environment, any forces which are not electrostatic by nature appear to be accounted for.

Further evidence of the point charge model's ability to represent the crystal environment is exhibited in the change in gross atomic population throughout the iterative cycles. There is a definite shift of electron density from the bridging

hydrogens to the acceptor atoms (O2/O2'), identical to those found in other ab initio studies of dimers.

My study proves that the calculated crystal structures are insensitive to the magnitude of the point charges. I conclude that the arbitrary assignment of charge by the Mulliken population analysis has a negligible effect on the point charge model.

SUGGESTIONS FOR FUTURE WORK

The remainder of this chapter is a short presentation of areas that I feel need further work.

Although the results of my study confirm the validity of the point charge model, the only types of crystals that have been tested to date involve hydrogen bonding. I strongly feel that further studies should be done on crystals bound together by both ionic and covalent bonds.

A quantitative method needs to be developed to treat the shift of electron density that frequently occurs in X-ray diffraction studies. Currently, no quantitative method exists and bond lengths determined by X-ray diffraction are often reported shorter than their actual value. The development of such a method is desperately needed to facilitate comparisons between calculated and experimental crystal structures.

The problems that I have presented with the neutron-diffraction study of H_2SO_4 by Moodenbaugh and coworkers point to repeating that study. The new study should incorporate the Yu and Mak data and be done on a single crystal if possible. As a minimum, Moodenbaugh's data should be refined again using the heavy atom positions from the 1978 X-ray study and anisotropic temperature

factors. I expect that the results of a new neutron-diffraction study will confirm that the S-O single bond length is closer to my calculated value than the X-ray value.

After discussions with several crystallographers, they all feel that a present day X-ray diffraction study of H_2SO_4 could locate the hydrogens. With the aid of a crystallographer, I have unsuccessfully tried to refine the Yu and Mak data to locate the hydrogens. Since no further knowledge can be gained from past X-ray diffraction studies, I feel a new X-ray study should be completed. The positions of the hydrogens, if located, can then be compared to the neutron-diffraction study to establish its accuracy.

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Vita

Mark Alan McCormick was born in Wilmington, Ohio on 27 November 1958, the son of Alice Ruth (Hutchison) McCormick and Clifford Allen McCormick. After moving throughout Ohio, he graduated from Findlay Senior High School, Findlay, Ohio in 1977. He was appointed by Congressman Tennyson Guyer and entered the United States Naval Academy (Annapolis) in July 1977. He graduated with Distinction on 27 May 1981 and received the degree of Bachelor of Science. On the same day, he was commissioned an Ensign in the United States Navy. After a personal interview with Admiral Hyman G. Rickover, he was selected to enter the Naval Nuclear Power Program in the spring of 1981.

Ensign McCormick was initially assigned TAD to the Naval Research Laboratory (NRL) in Washington, D.C. After working in the Theoretical Chemistry Section at NRL for five months, he reported to the Naval Nuclear Power School (NPS) located in Orlando, Florida in November 1981. After graduating near the top of his class, he reported to the S3G Naval Nuclear Prototype at Ballston Spa, New York in May 1982. After qualifying as Engineering Officer of the Watch (EOOW), he reported to the Submarine Officer's Basic Course (SOBC) in New London, Connecticut. He graduated with Distinction from SOBC in March 1983.

Ensign McCormick reported to the Blue Crew of the USS Simon Bolivar (SSBN-641), a Trident missile configured fleet ballistic missile submarine, homeported in Charleston, South Carolina in April 1983. He completed three strategic deterrent patrols and received his "Dolphins" in September 1984. During that time, he served as the Main Propulsion Assistant (MPA), Chemistry and

Radiological Controls Assistant (CRA), and Interior Communications Officer. In February 1985, Lieutenant McCormick passed his Engineer's Exam and was certified as an Engineering Officer of a Naval Nuclear Propulsion Plant. LT McCormick then returned to the USS Simon Bolivar which had commenced a nuclear refueling overhaul at the Portsmouth Naval Shipyard in Portsmouth, New Hampshire. He remained onboard for ten months serving as the Refueling Officer and Assistant Engineer. While assigned to the USS Simon Bolivar, LT McCormick was awarded two Navy Achievement Medals and a Commander Submarine Group SIX Commendation for his superior performance.

In January 1986, LT McCormick was ordered to the University of Texas and entered the graduate program. After completing his Master of Arts degree, LT McCormick will report to the Submarine Officers Advanced Course (SOAC) in New London, Connecticut and will subsequently be assigned to a submarine as either an Engineer or Navigator in Charleston, South Carolina.

Mark McCormick married Laura Lee Avrett on 26 November 1982 in Tuscaloosa, Alabama. They are expecting their first child in January 1988.

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